

SILICA, AMORPHOUS

7501

SiO₂

MW: 60.08

CAS: Table 1

RTECS: Table 1

METHOD: 7501, Issue 2

EVALUATION: PARTIAL

Issue 1: 15 May 1985

Issue 2: 15 August 1994

OSHA : Table 1

NIOSH: Table 1

ACGIH: Table 1

PROPERTIES: solid; d 2.2 g/mL; MP >1600 °C

SYNONYMS: fumed amorphous silica (Aerosil, silica aerogel, silicic anhydride); fused amorphous silica (Cab-o-sil, colloidal silica, diatomaceous earth); hydrated amorphous silica (Hi-sil)

SAMPLING		MEASUREMENT	
SAMPLER:	FILTER (Total) or CYCLONE + FILTER (Respirable) (10-mm cyclone, nylon, Higgins- Dewell (HD) + 5-µm PVC)	TECHNIQUE:	X-RAY POWDER DIFFRACTION
FLOW RATE:	1 to 3 L/min (total) or	ANALYTE:	cristobalite
NYLON CYCLONE:	1.7 L/min (respirable)	ASH:	low temperature plasma; acid wash; deposit on PVC filter
HD CYCLONE:	2.2 L/min (respirable)	XRD ANALYSIS:	XRD for quartz, cristobalite and tridymite before and after heating
VOL-MIN:	50 L	HEAT:	1500 °C, 2 h (fumed amorphous silica) or 1100 °C, 6 h (other amorphous silica); redeposit on Ag filter
-MAX:	400 L @ 5 mg/m ³ (limit to ≤ 2 mg dust on filter).	CALIBRATION:	standard suspensions of amorphous silica in 2-propanol, converted to cristobalite as for samples
SHIPMENT:	routine	RANGE:	0.2 to 2 mg per sample
SAMPLE STABILITY:	stable indefinitely	ESTIMATED LOD:	0.005 mg per sample
BLANKS:	2 to 10 field blanks per set	PRECISION ($\hat{S}_p$):	0.10 @ 0.4 to 5 mg; 0.33 @ 0.2 mg [1]
BULK SAMPLE:	high volume area air sample required		
ACCURACY			
RANGE STUDIED:	not studied		
BIAS:	not determined		
OVERALL PRECISION ($\hat{S}_{RT}$):	not determined		
ACCURACY:	not determined		

APPLICABILITY: The method is specific for amorphous silica in crystalline (e.g., quartz) matrices in the range 1 to 10 mg/m³ for a 200-L air sample. Amorphous silica usually contains some crystalline silica [2].

INTERFERENCES: Albite, ammonium phosphate, and tridymite interfere with the largest peak of cristobalite. Quartz and cristobalite are quantitated prior to heat treatment and subtracted from the final quantity of cristobalite. Alkali and alkaline earth oxides prevent 100% conversion; these are removed by acid-wash prior to heat treatment. XRD signal intensity is proportional to particle size; similar particle size of samples and standards is desirable.

OTHER METHODS: This method makes improvements in sample handling and quality assurance to P&CAM 316, which it replaces [3,4]. The XRD analysis steps are similar to those in Method 7500 (Silica, crystalline).

REAGENTS:

1. Amorphous silica standard appropriate to the air sample, i.e., one of the following:
 - a. fumed amorphous silica, grade M-5 or M-7 (Cabot Corp.);
 - b. gelled amorphous silica, grade CD806 (The PQ Corp.);
 - c. diatomaceous earth amorphous silica, grade 680 Multicel;
 - d. precipitated amorphous silica, grade EP22 or DENT1 (The PQ Corp.) or grade Zeothix 177 (J.M. Huber Corp.).

NOTE 1: Some gelled or precipitated amorphous silicas contain up to 7% moisture. Dry all amorphous samples overnight at 115 °C [5].

NOTE 2: XRD signal intensity is proportional to particle size. Sieve the standards (10- μ m sieve), if necessary, to match the particle size expected in the samples.

2. 2-Propanol, reagent grade.
3. Water, deionized.
4. Sodium chloride, reagent grade.
5. Hydrochloric acid, 2% (v/v). Dilute 20 mL conc. HCl to 1 L with deionized water.
6. Desiccant.

EQUIPMENT:

1. Sampler:
 - a. Total dust: 37-mm diameter, 5.0- μ m pore size, polyvinyl chloride filter (MSA, Gelman GLA-5000, or equivalent) supported with backup pad in a two-piece, 37-mm cassette filter holder (preferably, conductive) held together by tape or cellulose shrink band.
NOTE: Gelman VM-1 and Millipore BS filters are unacceptable because of high ash or amorphous silica content.
 - b. Respirable dust: PVC filter (1.a. above) plus cyclone, 10-mm nylon, Higgins-Dewell (HD), or equivalent with sampling head holder. Holder must keep the cassette, cyclone and coupler together rigidly so that air enters only at the cyclone inlet.
 - c. Area sample: PVC filter (1.a. above) at 3 L/min.
2. Personal sampling pumps: 1 to 3 L/min (total or area); 1.7 L/min (nylon cyclone) or 2.2 L/min (HD cyclone).
3. Filters, PVC, 25-mm diameter, 0.45- μ m pore size.
NOTE: These may be cut from acceptable 37-mm PVC filters (not Gelman VM-1 or Millipore BS) by cutting up to five filters, interleaved with separator papers, with a sharp, 25-mm cork borer.
4. Filters, silver membrane, 25-mm diameter, 0.45- μ m pore size (Poretics, Costar/Nuclepore, or equivalent).
5. X-ray powder diffractometer with copper target X-ray tube and scintillation detector.
6. Glue or tape for securing Ag filters to XRD holders.
7. Reference specimen (mica, Arkansas stone or other stable standard) for data normalization.
8. Low temperature plasma asher (LTA) or muffle furnace.
9. Filtration apparatus with side-arm vacuum flask and 25- and 37-mm filter holders.
10. Sieve, 10- μ m pore size, for wet sieving.
11. Furnace capable of maintaining 1100 °C for 6 h or 1500 °C for 2 h and of temperature programming to 500 °C at 50 °C/min.
12. Crucibles, platinum, with covers.
13. Analytical balance (0.01 mg).
14. Stirrer, magnetic, with thermally-insulated top.
15. Ultrasonic bath or probe.
16. Pipets, 2- to 25-mL.

EQUIPMENT - cont.:

17. Volumetric flasks, 1-L.
18. Desiccator.
19. Bottle, 1-L, with ground glass stopper.
20. Drying oven.
21. Wash bottle, polyethylene.
22. Mortar and pestle, agate.
23. Rubber policeman.
24. Beakers, 100-mL, with watchglass covers.

SPECIAL PRECAUTIONS: None.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Sample at 1 to 3 L/min (total and area), 1.7 L/min (nylon cyclone) or 2.2 L/min (HD) for a total sample size of 50 to 400 L.

NOTE: Do not allow the cyclone to be inverted at any time. Turning the cyclone more than 90 °C from vertical may deposit over-sized material from the cyclone body onto the filter.

SAMPLE PREPARATION:

3. Ash the sample filter in a 100-mL beaker in the LTA according to manufacturer's instructions. After ashing, carefully (so as to avoid loss of sample) add 50 mL 2% HCl to each beaker.
4. Cover the beaker with a watchglass. Agitate in an ultrasonic bath for at least 3 min (until the agglomerated particles are broken up). Wash the underside of the watchglass with distilled water, collecting the washings in the same beaker.
5. Place a 25-mm PVC filter in the filtration apparatus. Attach the funnel securely over the entire filter circumference. With no vacuum, pour 2 to 3 mL deionized water onto the filter. Pour the sample suspension from the beaker into the funnel, and apply vacuum. Rinse the beaker with deionized water and add rinsings to funnel. When filtration is complete, keep vacuum on until filter is dry. Remove the filter with forceps and attach it to the sample holder for XRD analysis.

NOTE: Control filtration rate to keep the liquid level in the funnel near the top during rinsing. Do not wash the walls or add deionized water to the funnel when the liquid level is lower than 4 cm above the filter.

CALIBRATION AND QUALITY CONTROL:

6. Weigh ca. 100 mg dried amorphous silica to the nearest 0.01 mg. Quantitatively transfer to a 1-L bottle using 1.00 L 2-propanol. The resulting concentration is 100 µg/mL.
7. Suspend the powder in 2-propanol using an ultrasonic probe or bath for 20 min. Immediately move the 1-L bottle to a magnetic stirrer with thermally-insulated top and add a stirring bar to the suspension. Allow the solution to return to room temperature before withdrawing aliquots.
8. Prepare a series of standard filters, in triplicate, over the range 0.005 to 2 mg per sample.
 - a. Mount a 37-mm PVC filter on the filtration apparatus. Add ca. 3 mL 2-propanol to wet the filter.
 - b. Shake the bottle vigorously by hand. Immediately remove the stopper and withdraw an aliquot (e.g., 2 to 25 mL) by pipet from the center of the suspension.

NOTE: Do not adjust the volume in the pipet by expelling part of the suspension. If more than the desired aliquot is withdrawn, return all of the suspension to the bottle, rinse and dry the pipet, and take a new aliquot.
 - c. Transfer the aliquot from the pipet to the filter. Keep the tip of the pipet near the surface but not submerged in the suspension. Rinse the pipet with ca. 5 mL 2-propanol, draining the

- rise into the funnel. Repeat the rinse three more times.
- d. Apply vacuum and rapidly filter the suspension. Keep vacuum on until the filter is dry. Do not wash down the sides of the funnel after the deposit is in place.
 9. Prepare and analyze standard filters exactly like samples.
 - a. Ash in LTA; redeposit on 25-mm PVC filters (steps 3 through 5).
 - b. Analyze by XRD (step 13).
 - c. Heat to convert amorphous silica to cristobalite; redeposit on Ag filters (steps 13 through 15).
 - d. Analyze by XRD (step 17).
 10. Prepare calibration graph ($\hat{I}_x$ vs. mg of standard).
 NOTE: Poor repeatability (i.e., $S_r > 0.1$) at any given level indicates that new standards should be made. The data should lie along a straight line. A weighted least squares ($1/S^2$ weighing) is preferable. Curvature can be eliminated with absorption corrections (step 20) [6].
 11. Select six silver membrane filters to be analyzed as media blanks. make the selection randomly from the same box of filters used for depositing samples. Mount each media blank on the filtration apparatus and apply vacuum to draw 5 to 10 mL of 2-propanol through the filter. Remove, let dry and mount on XRD holders. Determine net normalized intensity for the silver peak for each media blank.

MEASUREMENT:

12. Obtain a qualitative X-ray diffraction scan (broad 2θ range) of the bulk (high-volume respirable) sample to determine the presence of free silica polymorphs and any matrix interference. The diffraction peaks are:

<u>Substance</u>	<u>Peak (2-θ Degrees)</u>	
	<u>Primary</u>	<u>Secondary</u>
Quartz	26.66	20.85
Cristobalite	21.93	36.11
Tridymite	21.62	20.50
Silver	38.12	44.28

NOTE: For quantitative determination of amorphous silica in bulk samples, wet-sieve a portion of the bulk sample through a 10- μ m sieve with 2-propanol in an ultrasonic bath. Evaporate the alcohol and dry in an oven 2 h. Weigh out, in triplicate, 2-mg portions of the sieved dust and transfer to beakers. Add 10 mL 2-propanol, deposit on a PVC filter (step 5) and continue with steps 13 through 17.

13. Mount the filter (sample, standard, or blank) in the XRD instrument and perform the following:
 - a. Determine net intensity, I_r^o , of the reference specimen before filter is scanned. Select a convenient scale factor, N, which is approximately equivalent to the net count for the reference specimen peak; use this for all analyses.
 - b. Step-scan the most intense diffraction peak of each compound to be determined, integrating the counts.
 - c. Measure the background on each side of the peak for one-half the time used for peak scanning and add the counts from each side for a total (average) background.
 - d. Calculate net intensity, I_x , (the difference between the peak integrated count and the total background count).
 - e. Calculate and record normalized intensity, $\hat{I}_x$, for the sample peak on each sample, field blank, and standard:

$$\hat{I}_x = \frac{N}{I_r^o} \cdot I_x$$

NOTE: Normalizing to the reference specimen intensity compensates for long-term drift in X-ray tube intensity. If intensity measurements are stable, the reference specimen may be run less frequently and net intensities should be normalized to the most recently measured reference intensity.

14. Remove the PVC filter from the XRD holder, fold the filter carefully and place it in a platinum crucible in the furnace. Raise the temperature of the furnace slowly (ca. 50 °C/min) to 500 °C to ash the filter. When ashing is completed (ca. 0.5 h), raise the temperature to 1500 °C and maintain at 1500 °C for 2 h (for fumed amorphous silica) or to 1100 °C and maintain at 1100 °C for 6 h (for other amorphous silicas). Turn the furnace off and let the crucibles cool overnight in the furnace.
15. Place ca. 10 mg NaCl in the crucible and mix with the ash in the crucible. Transfer contents of the crucible to an agate mortar and grind to a fine powder using an agate pestle. Add distilled water from a polyethylene squeeze bottle to the mortar. Use a rubber policeman to stir. When the NaCl is dissolved, transfer the solution to a 100-mL beaker (hold the rubber policeman at the edge of the mortar to guide the flow into the beaker). Rinse mortar, pestle, crucible, and rubber policeman, collecting rinsings in the beaker. Cover the beaker with a watchglass and place in an ultrasonic bath for 2 to 3 min.

NOTE 1: Use extreme care to avoid air currents when working with the dry sample, as it is easily lost in the form of an aerosol.

NOTE 2: Use uniform grinding techniques to produce similar particle size in standards and samples.
16. Wash the underside of the watchglass and collect rinsings in the beaker. Place a silver membrane filter in the filtration apparatus and filter the contents of the beaker (step 5).
17. Mount the silver membrane filters in the XRD instrument and:
 - a. Analyze for the three silica polymorphs (step 13); and
 - b. Determine the net intensity, I_{Ag} , of an interference-free silver peak on the sample filter following the same procedure.

NOTE: Scan times should be shorter for the silver peak (e.g., about 5% of scan times for analyte peaks) and consistent throughout the method.

CALCULATIONS:

18. Calculate normalized intensities for the cristobalite peak on the PVC filter before heating, $\hat{I}_x$ (step 13); the cristobalite peak on the Ag filter, $\hat{I}'_x$ (step 17.a.); the silver peak on the Ag filter, $\hat{I}_{Ag}$ (step 17.b.); and the average silver peak on six media blank Ag filters, $\hat{I}_{Ag}$ (step 11).
19. Calculate the transmittance of each sample: $T = \hat{I}_{Ag} / \hat{I}'_{Ag}$.
20. Calculate the matrix absorption correction factor for each sample, $f(T) = -R \ln T / (1 - T^R)$, where $R = \sin(\Theta_{Ag}) / \sin(\Theta_x)$ (or use Table 1).
21. Calculate the concentration of amorphous silica, C (mg/m³), in the air sample as the difference in cristobalite concentrations measured before and after heat treatment using the slope, m , and intercept, b , of the calibration graph and the air volume sampled, V (L):

$$C = \frac{[(\hat{I}'_x - b) / m] f(T) - [(\hat{I}_x - b) / m] \cdot 10^3}{V}, \text{ mg/m}^3.$$

NOTE: Compute the applicable OSHA standard using the formulae on page 7501-1 and the % crystalline silica found in the air sample before heat treatment.

EVALUATION OF METHOD:

This method is based on NIOSH P&CAM 316 [3,4] which was further evaluated with field samples in July, 1982 [1]. The relative standard deviation was determined to be related to the type of amorphous silica; gelled, fumed, and precipitated amorphous silica yielded 4.4%, 8.2%, and 4.7%, respectively, over

the range of 0.5 to 5 mg. The method was further evaluated using 11 different types of gelled, precipitated, and fumed amorphous silicas and diatomaceous earth [5], with the following conclusions:

1. Not all fumed silicas converted to cristobalite at 1100 °C. A higher temperature (1500 °C) was needed to convert all the fumed silicas to cristobalite.
2. The moisture content of the gelled and precipitated silicas was ca. 7%; of diatomaceous earth, ca. 4%; and of fumed, from 0.5 to 3%.
3. The calibration curves from the four different types of amorphous silicas indicated very similar slopes ($S_r = \pm 6.6\%$).
4. Comparing the four slopes to a slope of a pure respirable cristobalite material, they were running approximately 30% lower in slope value. Therefore, field samples of amorphous silicas must be compared only to standards prepared from amorphous silicas.
5. Precision studies at 0.2-, 1-, and 2.5-mg levels (six samples per level) of gelled, precipitated, diatomaceous earth, and fumed silicas indicated a pooled precision, $\bar{S}_r$, of 8.8, 10.5, 5.6, and 21.5%, respectively, for the above silicas.
6. Recovery studies of the same silicas and concentration levels indicated average recoveries of 82, 115, 95, and 111%, respectively, with pooled $\bar{S}_r$ equal to 18.2, 13.1, 12.9, and 15.3%, respectively, for the gelled, precipitated, and fumed silicas, and diatomaceous earth.

REFERENCES:

- [1] Palassis, J. NIOSH Internal Report (August 1982).
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- [3] NIOSH Manual of Analytical Methods, 2nd ed., Vol. 6, P&CAM 316, U.S. Department of Health and Human Services, Publ. (NIOSH) 80-125 (1980).
- [4] Lange, B.A., J.C. Haartz, and R.W. Hornung. "Determination of Synthetic Amorphous Silica on Industrial Air Samples," *Anal. Chem.*, **53** (9), 1479-84 (1981).
- [5] Palassis, J. Amorphous Silica Analysis by X-Ray Diffraction Quantitative Analysis of Quartz in Industrial Dust Films Deposited on Silver Membrane Filters," *Occup. Health Rev.*, **21**:26 (1970).
- [6] Lerous, J. and C. Powers. "Direct X-Ray Diffraction Quantitative Analysis of Quartz in Industrial Dust Films Deposited on Silver Membrane Filters," *Occup. Health Rev.*, **21**:26 (1970).

METHOD REVISED BY:

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TABLE 1. CAS Numbers, RTECS Numbers, and Exposure Limits for Amorphorous Silica Forms

Amorphous Forms	CAS#	RTECS	OSHA PEL (mg/m ³)	NIOSH REL (mg/m ³)	ACGIH TLV (mg/m ³)
diatomaceous earth, <1% crystalline SiO ₂	61790-53-2	HL8600000	80/% SiO ₂	6	10 (total)
precipitated, and gel	7699-41-4, 112926-00- 8	VV8850000	80/% SiO ₂	6	10 (total)

fumed	112945-52- 5	VV7310000	80/% SiO ₂	--	2 (respir)
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Table 2. Matrix Absorption Correction Factors for Cristobalite (Heat-Converted Amorphous Silica) and Silver Peaks.

Cristobalite Silver	Degrees 2- Θ					
	21.93		21.93		21.93	
	38.12		44.28		38.12	
	T	f(T)	f(T)	T	f(T)	f(T)
	1.00	1.0000	1.0000	0.74	1.2806	1.3278
	0.99	1.0087	1.0100	0.73	1.2944	1.3440
	0.98	1.0174	1.0201	0.72	1.3084	1.3605
	0.97	1.0264	1.0305	0.71	1.3226	1.3774
	0.96	1.0355	1.0410	0.70	1.3372	1.3946
	0.95	1.0447	1.0517	0.69	1.3521	1.4122
	0.94	1.0541	1.0625	0.68	1.3673	1.4303
	0.93	1.0636	1.0736	0.67	1.3829	1.4487
	0.92	1.0733	1.0849	0.66	1.3987	1.4675
	0.91	1.0831	1.0963	0.65	1.4150	1.4868
	0.90	1.0932	1.1080	0.64	1.4316	1.5064
	0.89	1.1034	1.1199	0.63	1.4485	1.5266
	0.88	1.1137	1.1320	0.62	1.4659	1.5472
	0.87	1.1243	1.1443	0.61	1.4836	1.5684
	0.86	1.1350	1.1568	0.60	1.5018	1.5900
	0.85	1.1460	1.1696	0.59	1.5204	1.6122
	0.84	1.1571	1.1827	0.58	1.5394	1.6349
	0.83	1.1685	1.1959	0.57	1.5590	1.6582
	0.82	1.1800	1.2095	0.56	1.5790	1.6820
	0.81	1.1918	1.2232	0.55	1.5995	1.7065
	0.80	1.2038	1.2373	0.54	1.6205	1.7317
	0.79	1.2160	1.2516	0.53	1.6421	1.7575
	0.78	1.2284	1.2663	0.52	1.6642	1.7840
	0.77	1.2411	1.2812	0.51	1.6870	1.8112
	0.76	1.2540	1.2964	0.50	1.7103	1.8391
	0.75	1.2672	1.3199			